Decomposition of Nitroplasticizer in Plastic-Bonded Explosive PBX 9501

Denise K. Pauler (T-12 and Cornell University) and Joel D. Kress (T-12)

The goals of the Constituent Aging Study (CAS) are to investigate the accelerated aging of various constituents of plastic-bonded explosive PBX 9501, detect chemical reactions that occur, and identify decomposition products and possible mechanisms for chain scissioning and crosslinking of the polyester (urethane) Estane® 5703 [1]. The constituents of PBX 9501 are HMX explosive crystals, Estane®/nitroplasticizer (NP) binder, and diphenylamine or Irganox stabilizer. The NP, a liquid consisting of a 50/50 mixture (by wt.) of bis-2,2-dinitropropyl acetal (BDNPA) and formal (BDNPF), softens the Estane®, and together this binder markedly decreases the mechanical sensitivity of PBX 9501. Experimental evidence from NMR and ESR spectroscopy strongly suggests that NP degradation products may attack the Estane® and oxidize the polyurethane segment. Very little is known of the mechanisms for the oxidation of polymers by oxidants other than molecular oxygen. As the first step in the aging of PBX 9501 in a low moisture and low oxygen environment, we propose that NP decomposes into oxidizing gasses (NO_2 and NO). In this report, we present a plausible reaction mechanism for the decomposition of NP based on: (1) the results of the CAS, (2) an existing mechanism for liquid nitroethane, and (3) density functional electronic structure calculations.

During the 3-year duration of the CAS, the accelerated aging was performed in a dry oxygen-free environment at various temperatures (48°, 56°, and 64°C). Over one thousand samples were analyzed for small molecule reaction products such as CO_2, N_2O, Ar, O_2, NO, N_2, CO, H_2, and small organics. For example, the amount of N_2O,

NO, CO, and CO_2 gas evolved as a function of time for a sample of pure NP aged at 64°C is shown in Fig. 1. The amount of N_2O and NO gas evolves at a nearly constant rate from time zero to approximately 120 weeks, whereas the CO and CO_2 gas evolution appears to have a delayed threshold starting at 26 weeks. One goal is to explain this result from our theoretical investigation of NP.

To minimize the computational effort for the electronic structure calculations, 2,2-dinitro-1-methoxypropane (first molecule in Scheme 1) was chosen as a model compound since it resembles half of the NP molecule. A library of key reactions was prepared and the electronic structure studied using the *Gaussian 03* suite of programs. The relative energies ΔE (products relative to reactants) were calculated using the hybrid density functional B3LYP and a 6-31G(d,p) basis set. Melius and Piqueras proposed a mechanism for the decomposition of nitroethane, a compound similar but less complex than NP. There are two potential pathways to begin the mechanism. The first is NO_2 scission, where the activation energy is equivalent to the bond dissociation energy. The second is a five-centered HONO elimination, which has a lower activation energy than NO_2 scission. While NO_2 scission dominates at high temperatures, as evidenced by the kinetics studies on nitromethane and nitropropane by Zhang and Bauer, the HONO elimination dominates at low temperatures of relevance to the CAS and naturally aged PBX 9501.

A series of five reactions (Scheme 1) for the decomposition mechanism of NP were selected from the library of reactions as follows. There are three possible products resulting from HONO elimination, but only two result in substituted alkenes and are therefore lower in energy. The *trans* HONO elimination product (first step in Scheme 1, $\Delta E = -3$ kcal/mol) is chosen since it is more stable due to steric hindrance in the cis alkene. After the elimination step, HONO remains trapped in the liquid and then adds to the alkene backbone of the NP fragment. HONO readdition can lead to various structural isomers depending on whether the H-ONO or HO-NO bond is broken. Addition of HO-NO leads to a nitroso-alcohol compound (second step in

Scheme 1, $\Delta E = -4$ kcal/mol) which decomposes (third step in Scheme 1, $\Delta E = -31$ kcal/mol) to produce methyl formate and a nitro-oxime. Esters can react further to produce CO and CO_2 (final step in Scheme 1, $\Delta E = 22$ and -23 kcal/mol, respectively), which were observed in the CAS study (Fig. 1). The nitro-oxime can decompose into acetaldehyde and NO, the latter which may account for the N_2O and NO gasses observed in the CAS study (Fig. 1).

In conclusion, the key reactions involved in the decomposition of NP, including NO_2 scission and HONO elimination, have been identified. A proposed mechanism for low temperatures illustrated that HONO elimination can lead to esters that react further to produce CO and CO_2 gasses, and to nitro-oximes that can decompose into oxidizing gasses (NO). The next goal is to investigate NP decomposition kinetics with detailed Estane® polymer chain scission and crosslinking kinetics.

[1] J.D. Kress, et al., *34th Annual PolyMAC Symposium*, Albuquerque, NM, June 8–10, 2004, book of abstracts, p. 18.

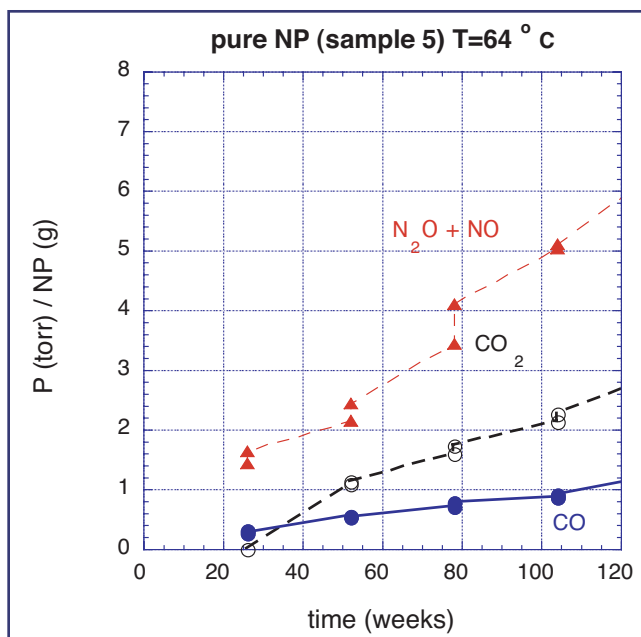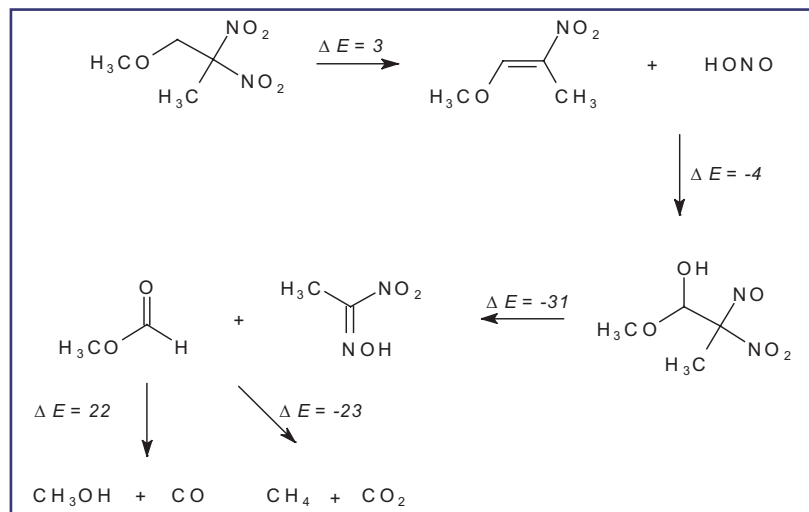*For more information, contact Denise K. Pauler (dkpauler@lanl.gov).*

Figure 1—
Gas (partial pressure) evolved per gram of nitroplasticizer (NP) aged at 64˚C.

Scheme 1—
Proposed mechanism for nitroplasticizer (NP) model compound. Energies in kcal/mol.